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A METHOD FOR THE DETECTION OF SMALL QUANTITIES OF COUMARIN, PARTICULARLY IN FACTITIOUS VANILLA EXTRACTS.

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The search for a delicate test for coumarin was prompted by two sets of circumstances: (1) The methods heretofore proposed have proved unreliable for detecting small amounts, and (2) an examination of the records of various food-inspection departments, State and Federal, shows that rarely in recent years has coumarin been found in vanilla extracts unless its presence was declared on the label. For this reason the two extractions by the Hess-Prescott method, which have for their object the separation of coumarin from vanillin, are usually superfluous. These extractions are time consuming and exacting, and hence, if they may be in the majority of cases omitted, a decided advantage is gained.

It is known that when coumarin is fused with potassium hydroxid, potassium salicylate is formed. Vanillin under these conditions forms the potassium salt of protocatechuic acid. If a mixture of vanillin and coumarin is fused with potassium hydroxid the ferric salt test for salicylic acid is hidden by the color produced by the protocatechuic acid. Ferric chlorid forms at first a wine color in the alkaline solution of the latter acid. This color changes through purple, blue, and green to colorless on the addition of acid. Protocatechuic acid, however, will not distill over with steam, as is the case with salicylic acid. Upon the foregoing facts the following method for the detection of coumarin in factitious vanilla extracts is based:

Slightly acidify 25 cc of the extract, if alkaline, with sulphuric acid, add 25 cc of water, and distill to dryness. To the distillate, containing the vanillin and coumarin, add 15 to 20 drops of 1:1 potassium hydroxid, hastily evaporate the distillate to 5 cc, and

transfer to a test tube. Heat the test tube over a free flame until the water completely evaporates and the residue fuses to a colorless, or nearly colorless, mass. The reaction previously described will have occurred. Cool the melt and dissolve in a few cubic centimeters of water. Transfer the solution to a 50 cc Erlenmeyer flask and acidify slightly with 25 per cent sulphuric acid. The amount of solution should not be over 10 cc. Finally distill the solution into a test tube containing four or five drops of neutral 0.5 per cent ferric sulphate or ferric chlorid. If coumarin is present in the original extract, an amethyst or purplish color will develop, the intensity being directly proportional to the amount of coumarin.

Vanillin and other normal constituents of vanilla extract do not interfere. The former substance is transformed, as stated, into protocatechuic acid, which does not distill over. Abnormal ingredients which would form salicylic acid under similar conditions, saccharin for example, would prove misleading. Protocatechuic and salicylic acids can also be separated by benzol, the latter acid being soluble, thus rendering possible the detection of coumarin. To the benzol solution of the salicylic acid, obtained as described above, a few drops of a ferric salt and about 1 cc of water are added and the mixture shaken. The solution beneath the benzol will be colored purple if coumarin was originally present.

This reaction is very delicate. If pure coumarin is used, 0.1 mg can be readily detected by adding the ferric salt to the alkaline solution, and then 2 per cent acid, and finally tenth normal acid to neutralization or development of maximum color. One milligram will give a striking purplish color. One milligram of coumarin and 50 mg of vanillin will give a distinct purplish color when the separation is made by the distillation method, as just outlined. Twenty-five cubic centimeters of an extract containing 0.005 per cent of coumarin will give quite a marked amethyst color. This method was tested on numerous vanilla extracts of known composition, and in no case was a color developed when the extract contained no coumarin. In the case of a factitious extract containing 0.04 per cent coumarin the color developed was a deep purple; by reflected light, almost black.

This method furnishes a quick qualitative test, inasmuch as it takes less than half an hour. Obviously it will shorten the provisional method of the Association of Official Agricultural Chemists for vanillin and coumarin in extracts. If no coumarin is found to be present by this method it will be necessary to make only the first ether extraction, thereby doing away with the possible error due to the other two. These same reactions might be used for the quantitative estimation of small amounts of coumarin. The details of the quantitative estimation are the subject of further study.